



Inorganic Chemistry

Programme Code- MSCCH-17/18/19

Course Code-CHE-501

**Unit 13 : Substitution Reaction Mechanisms of Square
Planar complexes**

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LEARNING OUTCOMES:

After studying this chapter, you will be able to-

- Understand the substitution in Square Planar Complexes
- Stereochemistry involve in the substitution in Square Planar Complexes
- Factors affecting Substitution in Square Planar complex

❖ NUCLEOPHILIC SUBSTITUTION REACTIONS OF SQUARE

PLANNER COMPLEXES

Before starting the study on mechanism of ligand substitution reactions in coordination compounds the following terms should be defined.

➤ **Transition state or activated complex:**

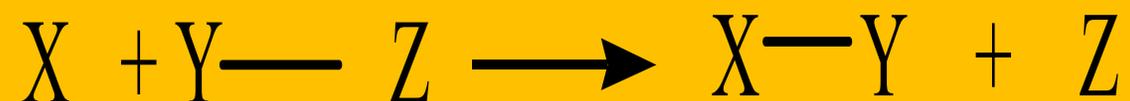
Let us consider the energy changes occurring during the course of the reaction.



Initially both X and Y-Z possess certain amount of potential energy represented by the point on the curve shown in increase in the potential energy until a critical energy state (which is y-z bond is weakened and ultimately the products, X-Y and Z are formed as shown at point (c) in fig. in given figure. In this process the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy. Fig. (a) illustrates that for an exothermic reaction the reactants originally possess more potential energy than the products and excess energy ($+\Delta H$) is liberated as heat. Fig. (b) shows that for an endothermic reaction the reactants have less potential energy than the products and, therefore the reactants absorb heat equal to H from the surroundings during their change into products.

Obviously ΔH is the energy difference between the reactants and the products. It is called reaction energy.

The reaction,



The above reaction can take place by the following steps:

The molecule X approaches Y-Z from a direction remote from Z. While X draws nearer to Y, Z starts being repelled from Y until a stage is reached in which X and Z are rather loosely attached to Y and approximately equidistant from it. In this stage the species X...Y.....Z are formed. This species is called the transition state or activated complex which has the following characteristics.

1. In this X to Y and Y to Z distances are slightly greater than the normal bond lengths
2. It is not a true molecule, the bonds being partial. Thus it is of a transitory nature and refers to an imaginary molecule and hence cannot be isolated.
3. It has the maximum energy and hence is the most unstable and has very-very short life time. The activated complex which is the most unstable changes to give the products X-Y and Z. Thus the various steps responsible for the reaction are:



The difference in energy between the reactants and the activated complex is called activation energy:

Energy changes in exothermic and endothermic reactions:

The energy changes in exothermic and endothermic reactions can be represented as:

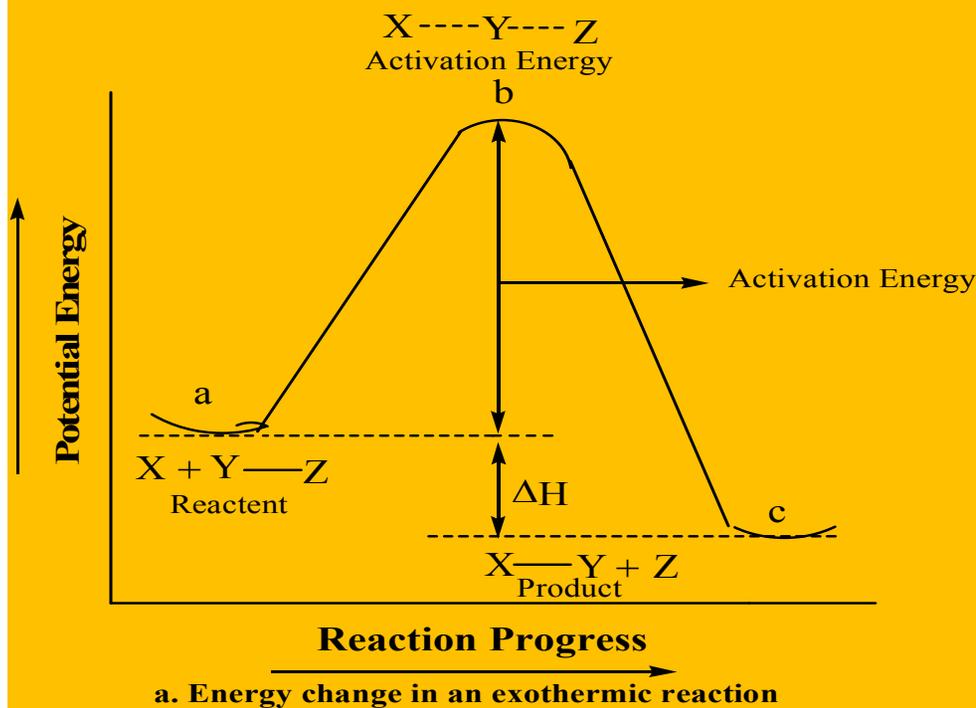


Figure: 1

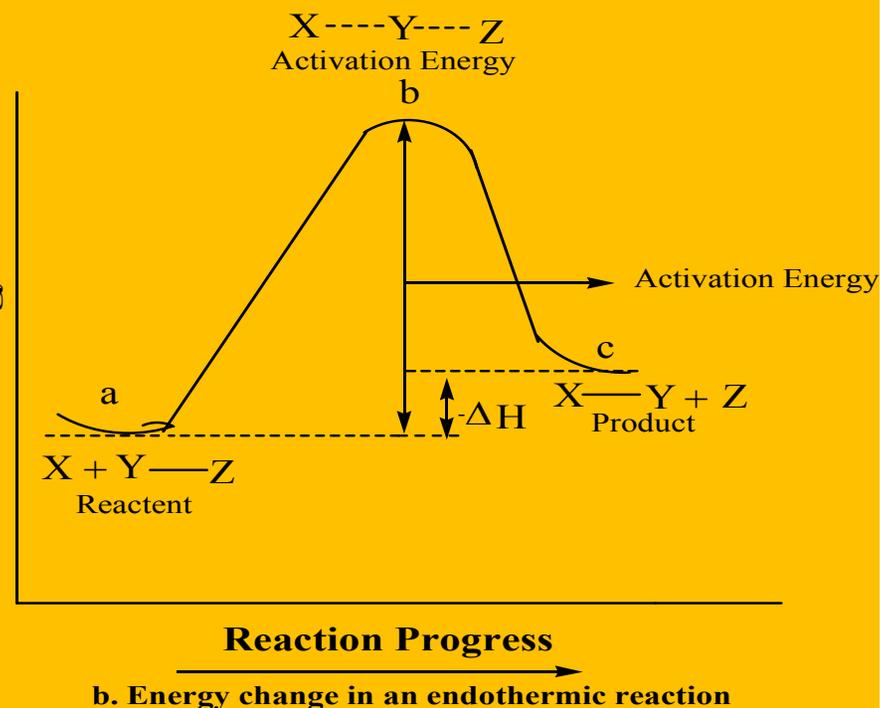


Figure: : 2

➤ **Substrate:**

A substrate may be defined as the reactant in which some bonds are broken and some new ones are formed as a result of the attack of a reagent.

➤ **Attacking reagents:**

We have mentioned above that a reaction proceeds when a reagent attacks on a substrate. These reagents are called attacking reagents and are of two types:

1. Electrophilic reagents
2. Nucleophilic reagents

1. ELECTROPHILIC REAGENTS:

These are also called electrophiles. As signified by the name electrophilic (electro means electron, philic means loving) these are electron loving (electron-seeking) or electron pair acceptor, since these are deficient by two electrons. Thus these are acceptor, since these are deficient by two electrons. Thus these are Lewis acids. These may be positively charged ions like carbemium ion C^+ , bromonium ion (Br^+), nitronium ion (NO_2^+), nitrosonium ion (NO^+), diozonium ion ($\text{C}_6\text{H}_5\text{N}_2^+$), bisulphonium ion (SO_2OH^+), proton (H^+), hydronium (H_3O^+) or neutral molecules such as BF_3 , AlCl_3 , SO_3 , FeCl_3 etc.

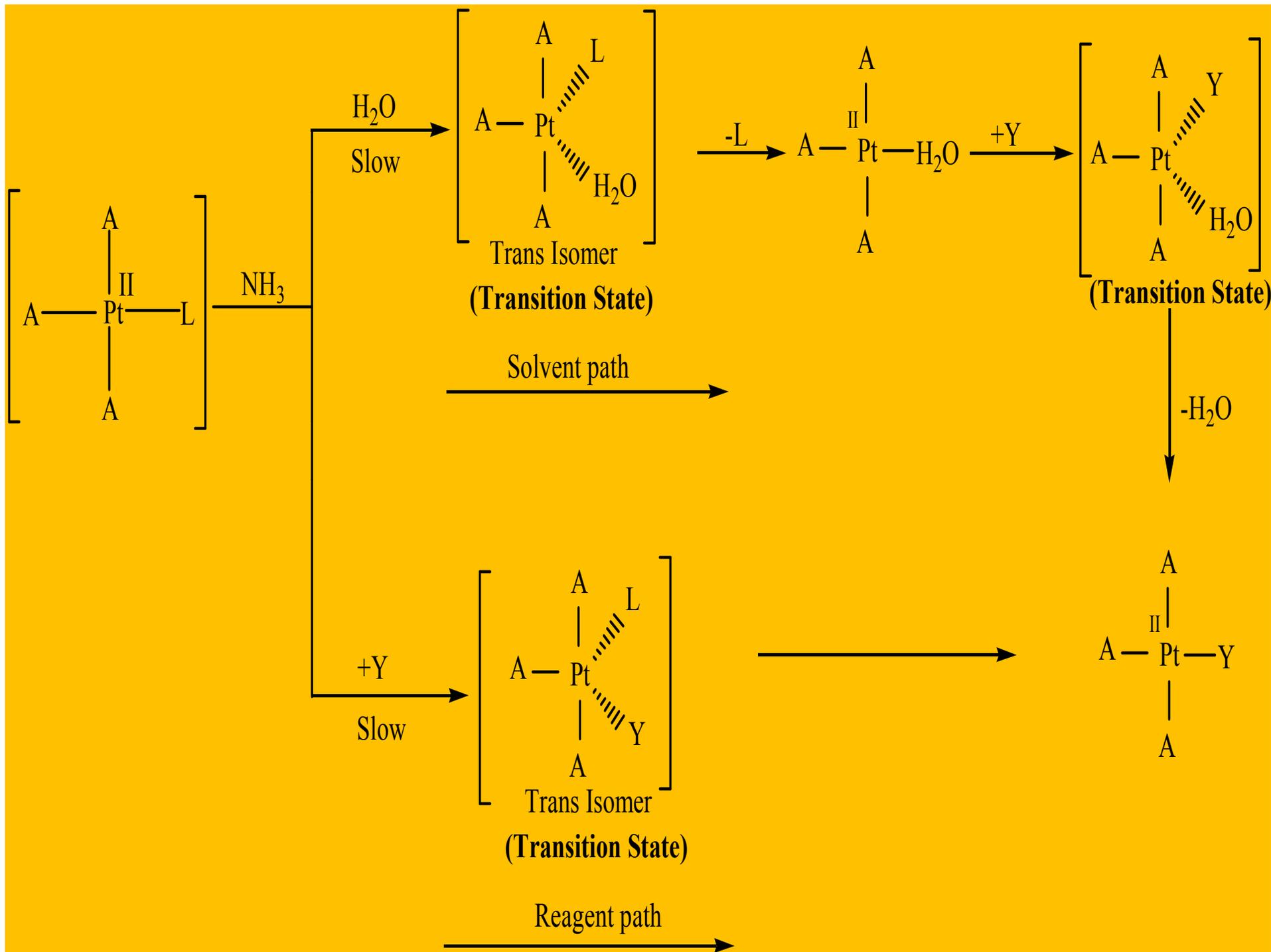
2. NUCLEOPHILIC REAGENTS:

These are also called nucleophiles (nucleo means nucleus, philic means loving these reagents are nucleus-loving (nucleus-seeker). Since the nucleus is electrically positive, the nucleophiles are electrically negative ions like carbanion, chloride ion (Cl^-), hydroxide ion (OH^-), cyanide ion (CN^-), bisulphide ion (SH^-), hydride ion (H^-) or electron-rich neutral molecules such as NH_3 , H_2O . Since these have unshared pair of electrons, these are Lewis bases (i.e., electron pair donor.) In coordination chemistry the central metal ion is an electrophile, since it accepts an electron pair while the ligands are nucleophiles because these donate electron pairs.

❖ **NUCLEOPHILIC SUBSTITUTION REACTIONS (SN_2)**
IN SQUARE PLANNER COMPLEXES:

When the Pt (II) square planner complexes undergo nucleophilic substitution reaction with the various ligand then sub reaction occur by the SN_2 mechanism through the two different path, which are known as solvent path & reagent path.

Nucleophilic substitution reaction in the $[Pt^{II}A_3L]$ square planner complex by the SN_2 mechanism through the solvent path & reagent path can be represented as:



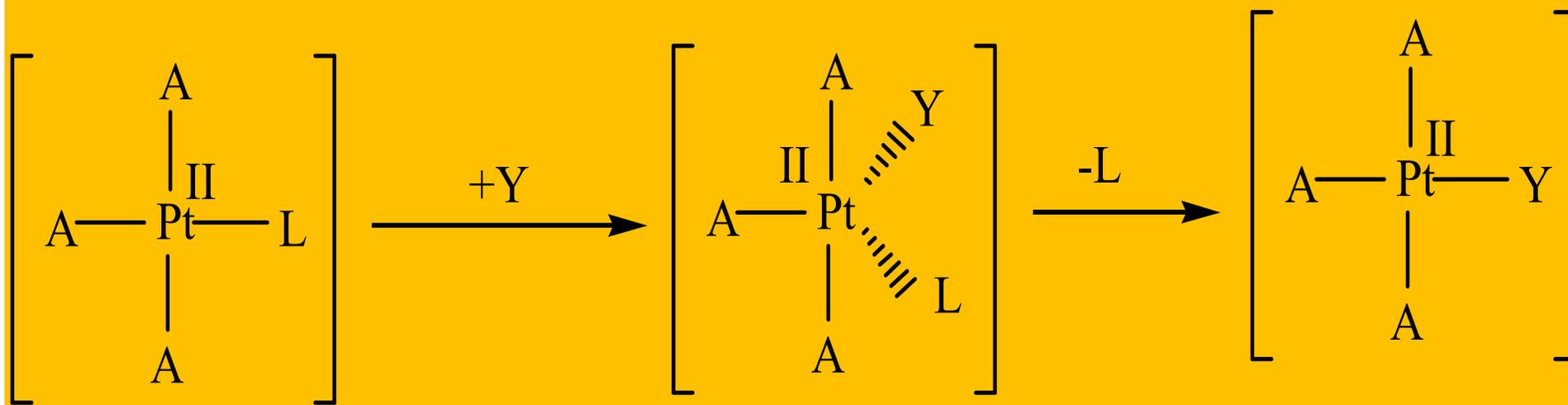
❖ FACTOR AFFECTING THE SN_2 REACTION OF SQUARE

PLANNER COMPLEXES:

Some of the factors which can affect the rate of the SN_2 reaction in the square planner complexes are given below:

1. Trans Effect:

In the Pt(II) square planner complexes with the increase in the trans effecting power of ligand (A) present in the trans position of leaving ligand (L), the rate of SN_2 reaction is increases.



Where $A = C_2H_4, NO_2^-, Br^-, Cl^-$

$L = F^-$

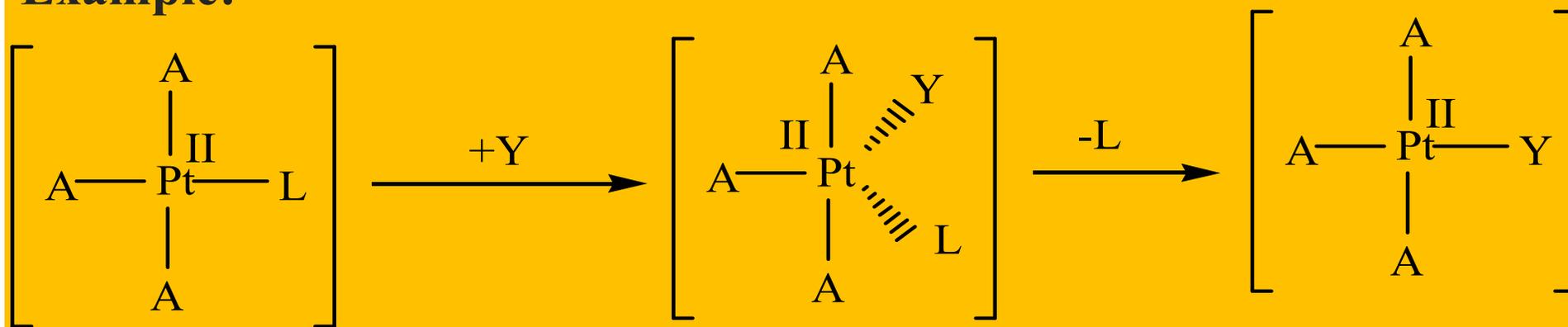
Trans effecting power of A = $C_2H_4 > NO_2^- > Br^- > Cl^-$

Rate of SN_2 reaction = $C_2H_4 > NO_2^- > Br^- > Cl^-$

2. Nature of leaving ligand (L):

With the increase The trans effecting power of leaving ligand (L) it's bonding with CMA become more and more stable by which it's rate of replacement is decreases.

Example:



Where $A = C_2H_4$

$L = PR_3, NO_2^-, Br^-, Cl^-, F^-$

Trans effecting power of L = $PR_3 > NO_2^- > Br^- > Cl^- > F^-$

Rate of SN_2 reaction = $PR_3 > NO_2^- > Br^- > Cl^- > F^-$

3. Effect of solvent:

It has been observed that the coordination ability of the solvent can easily compete with the of substitution reactions.



Some of the solvents have good coordinating ability hence these solvents doesn't affect the substitution of Cl^- ions. Like DMSO, H_2O and ROH etc. While some of solvent having weaker coordinating ability like CCl_4 , Benzene, acetone, DMF etc. In these solvents substitution reaction is

4. Effect of charge on complex:

An increase in the positive charge on the complex specie decreases rate of substitution reactions. The decrease in reaction rate is observed as the charge of the complex increases, a dissociative nucleophilic substitution SN1 process seems to be operative.

THANK YOU